UNIVERSITY OF PENNSYLVANIA

THE DISSOCIATION OF WATER IN POTASSIUM AND SODIUM BROMIDE SOLUTIONS

GEOFFREY M. JAMES

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA
1926

THE DISSOCIATION OF WATER IN POTASSIUM AND SODIUM BROMIDE SOLUTIONS

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

GEOFFREY M. JAMES

Reprint from
THE JOURNAL OF PHYSICAL CHEMISTRY, Vol. XXX, No. 8

PHILADELPHIA
1926

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Herbert S. Harned, under whose direction this investigation was carried out, and to Mr. Stuart D. Douglas who rendered valuable assistance in taking the readings.

R. UNIV.
BIBLIOTHEEK
LEIDEN

THE DISSOCIATION OF WATER IN POTASSIUM AND SODIUM BROMIDE SOLUTIONS*

BY GEOFFREY M. JAMES

In the present investigation, the method used by Harned, Harned and Swindells, and Åkerlöf[1] for the determination of the activity coefficient of water as an electrolyte and therefrom its dissociation in neutral aqueous potassium, sodium, lithium chloride and sulphate solutions has been used for determining these same quantities in aqueous potassium and sodium bromide solutions. The data necessary for the evaluations of these quantities include measurements of the cells:

$H_2 \mid HBr(m_o), MBr(m) \mid AgBr \mid Ag,$

$H_2 \mid MOH(m_o), MBr(m) \mid M_xHg \mid MOH(m_o) \mid H_2$, and

$Ag \mid AgBr \mid MBr(m+m_o) \mid M_xHg \mid MBr(m_o) \mid AgBr \mid Ag.$

In this study, measurements of the first of these cells containing 0.01 M and 0.1 M hydrobromic acid in potassium and sodium bromide solutions and measurements of the second of the above cells containing 0.1 M potassium hydroxide in potassium bromide solutions have been made. The necessary data on cells containing sodium hydroxide in sodium bromide solutions as well as the data for the third type of cells containing sodium bromide have been obtained from the yet unpublished work of Mr. Stuart D. Douglas. The data of the third type of cells containing potassium bromide were obtained from the measurements of Pearce and Hart,[2] supplemented by some values for the concentrated solutions obtained by Mr. Douglas.[3]

(1) Materials

Potassium amalgam containing 0.01% potassium was made by the method described by MacInnes and Parker, Knobel, and Harned.[4]

Potassium hydroxide solutions were prepared from the purest grade of potassium hydroxide available by precipitating the carbonate present in a solution of about 20% strength by means of a saturated solution of barium hydroxide. The carbonate-free solution was titrated against standardized hydrochloric acid, diluted to 0.1 M by redistilled water, and finally titrated from time to time with a 0.1 M hydrochloric acid solution which had been standardized gravimetrically. It was preserved in a large bottle fitted with soda-lime tubes.

Potassium and sodium bromides and potassium iodide of the best grade obtainable were ground and dried at 105°. These were tested for neutrality.

---

* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] Harned: J. Am. Chem. Soc., **47**, 930 (1925); Harned and Swindells: **48**, 126 (1926); Åkerlöf: **48**, 1160 (1926).

[2] Pearce and Hart: J. Am. Chem. Soc., **43**, 2483 (1921).

[3] Douglas: Thesis, University of Pennsylvania (1926).

[4] MacInnes and Parker: J. Am. Chem. Soc., **37**, 1445 (1915); Knobel: **45**, 70 (1923); Harned: **47**, 676 (1925).

Hydrobromic acid. Stock solutions of 0.01 M and 0.1 M acid were made and standardized by gravimetric analysis. The acid solutions containing the bromides were made from these solutions by adding to weighed portions the calculated amounts of the respective salts.

Hydrogen was prepared by electrolyzing a 15% sodium hydroxide solution in a suitable apparatus containing a nickel cathode and a platinum anode.

(2) Experimental Procedure

(a) *Cells:*

$$H_2 \mid HBr(m_o), MBr(m) \mid AgBr \mid Ag$$

Measurements of cells of this type containing no salt and different hydrobromic acid concentrations have been obtained by Lewis and Storch[1] and more recently by Livingston.[2] The electromotive forces of similar cells containing hydrochloric acid of constant strength and chloride solutions of varying strength have been studied extensively,[3] and the technique need not be described in detail. Suffice it to say that the method of preparing silver—silver chloride electrodes employed by Noyes and Ellis[4] was found to be quite satisfactory for the preparation of the silver—silver bromide electrodes. The measurements were all carried out at 25°. The electromotive forces were corrected to a hydrogen pressure of one atmosphere.

(b) *Cells:*

$$H_2 \mid KOH(m_o), KBr(m) \mid K_xHg \mid KOH(m_o) \mid H_2$$
$$H_2 \mid KOH(m_o), KI(m) \mid K_xHg \mid KOH(m_o) \mid H_2$$

Flowing amalgam cells of this type have been recently studied by a number of investigators.[5] In the present study, the cell employed was the same design as that described by Åkerlöf and permitted washing and filling without removal from its position in the thermostat. The solutions were boiled in vacuum and vacuum technique was employed throughout in the manner described by the previous investigators. This insured the removal of all but the slightest traces of dissolved air from the apparatus and the solutions.

(3) Measurement of the Cells

$$H_2 \mid HBr(m_o), MBr(m) \mid AgBr \mid Ag$$

and Discussion of the Activity Coefficient of Hydrobromic Acid in Potassium and Sodium Bromide Solutions.

If the electromotive force, E, of the above cell containing salt at a concentration (m) be subtracted from the electromotive force, E_o, of the same cell containing no salt and acid at a concentration (m_o), the electromotive force of the concentration cell without liquid junction, or

$$Ag \mid AgBr \mid HBr(m_o), MBr(m) \mid H_2 \mid HBr(m_o) \mid AgBr \mid Ag$$

[1] Lewis and Storch: J. Am. Chem. Soc., **39**, 2544 (1917).

[2] Livingston: J. Am. Chem. Soc., **48**, 45 (1926).

[3] Harned: J. Am. Chem. Soc., **38**, 1986 (1916); **42**, 1808 (1920); **48**, 326 (1926); Harned and Brumbaugh: **44**, 2729 (1922); Harned and Swindells: **48**, 126 (1926).

[4] Noyes and Ellis: J. Am. Chem. Soc., **39**, 2532 (1917).

[5] Knobel: J. Am. Chem. Soc., **45**, 70 (1923); Harned: **47**, 676 (1926); Harned and Swindells: **48**, 126 (1926); Åkerlöf: **48**, 1160 (1926).

is obtained. From this measurement, the free energy change of transfer from the acid to the acid—salt solution may be obtained and also the activity coefficient of the acid relative to its value at (m_o) concentration by the equation

$$-\frac{\Delta\bar{F}}{NF} = E_o - E = E' = 0.05915 \log \frac{\gamma_{H(s)}\gamma_{Br(s)}(m+m_o)m_o}{\gamma_{H(m_o)}\gamma_{Br(m_o)}m_o^2} \qquad (1)$$

whence, taking the square root of the fraction and rearranging,

$$\log \frac{\gamma_{HBr(s)}}{\gamma_{HBr(m_o)}} = \frac{E'}{0.1183} - \log\sqrt{\frac{(m+m_o)}{m_o}} \qquad (2)$$

is obtained since γ_{HBr} equals $\sqrt{\gamma_H\gamma_{Br}}$. Tables I and II contain the data and the activity coefficients of the hydrobromic acid for the solutions containing the acid at 0.01 M and 0.1 M concentrations and potassium bromide, and for the 0.01 M and 0.1 M acid solutions containing sodium bromide, respectively. The activity coefficient of the acid was taken to be 0.914 at 0.01 M pure aqueous solution. All other values of γ in the tables are referred to this one.

TABLE I

Activity Coefficients of Hydrobromic Acid in Potassium Bromide Solutions

$m_o = 0.1 \quad \gamma_o = 0.805$

m	E	E′	γ
0.0	0.20050*	0.00000	0.805
0.1	0.18532	0.01518	0.765
0.2	0.17611	0.02439	0.747
0.3	0.16922	0.03128	0.740
0.5	0.15924	0.04126	0.734
1.0	0.14218	0.05832	0.755
2.0	0.11948	0.08102	0.850
3.0	0.10234	0.09816	0.977

*Mean value of three determinations.

$m_o = 0.01 \quad y_o = 0.914$

m	E	E′	γ
0.0	0.31342†	0.00000	0.914
0.007	0.30107	0.01235	0.891
0.01	0.29730	0.01612	0.884
0.02	0.28792	0.02550	0.867
0.04	0.27637	0.03705	0.840
0.07	0.26573	0.04769	0.817
0.1	0.25869	0.05473	0.799
0.2	0.24400	0.06942	0.770
0.3	0.23530	0.07812	0.751
0.5	0.22295	0.09047	0.744
1.0	0.20466	0.10876	0.755
2.0	0.18130	0.13212	0.843
3.0	0.16384	0.14958	0.968

*Mean value of five determinations.

TABLE II

The Activity Coefficients of Hydrobromic Acid in Sodium Bromide Solutions

$m_o = 0.1$ $\gamma_o = 0.805$

m	E	E′	γ
0.0	0.20050	0.00000	0.805
0.1	0.18478	0.01572	0.773
0.2	0.17509	0.02541	0.762
0.3	0.16790	0.03260	0.759
0.5	0.15676	0.04374	0.770
1.0	0.13753	0.06297	0.827
2.0	0.11001	0.09049	1.022
3.0	0.08742	0.11308	1.306

$m_o = 0.01$ $\gamma_o = 0.914$

m	E	E′	γ
0.0	0.31342	0.00000	0.914
0.007	0.30094	0.01248	0.893
0.01	0.29711	0.01631	0.888
0.02	0.28771	0.02571	0.870
0.04	0.27625	0.03717	0.842
0.07	0.26538	0.04804	0.823
0.1	0.25854	0.05488	0.802
0.2	0.24337	0.07005	0.780
0.3	0.23412	0.07930	0.768
0.5	0.22112	0.09230	0.771
1.0	0.20047	0.11295	0.819
2.0	0.17207	0.14135	1.009
3.0	0.14925	0.16417	1.286

The activity coefficients of hydrobromic acid at 0.01 M and 0.1 M in potassium and sodium bromide solutions are plotted in Fig. 1 along with similar results for hydrochloric acid in potassium chloride solutions obtained from the data of Harned.[1] The activity coefficient of hydrobromic acid is greater in sodium than in potassium bromide solutions of equal strength which is similar to the behavior of hydrochloric acid in the corresponding chloride solutions. Further, the activity coefficient of hydrobromic acid in a bromide solution is greater than that of hydrochloric acid in the corresponding chloride solution. Since the activity coefficient of a pure bromide in aqueous solution is greater at a given concentration than the corresponding chloride, this follows the general rule that the activity coefficient of an acid—in contradistinction to an hydroxide—is greater in a solution containing a salt which has the greater activity coefficient. Finally, it is of interest to note that the curves of the 0.01 M series and the 0.1 M series are very nearly the same in all cases

[1] Harned: J. Am. Chem. Soc., **48**, 326 (1926).

at the same total concentration. This would indicate that the law of the linear variation of the logarithm of the activity coefficient is not exactly valid for hydrobromic acid in these bromide solutions.[1]

(4) Measurements of the Cells

$H_2 \mid KOH(m_2), KBr(m) \mid K_xHg \mid KOH(m_1) \mid H_2$

$H_2 \mid KOH(m_2), KI(m) \mid K_xHg \mid KOH(m_1) \mid H_2$

and the Activity Coefficients of Potassium Hydroxide in Potassium Bromide and Iodide Solutions.

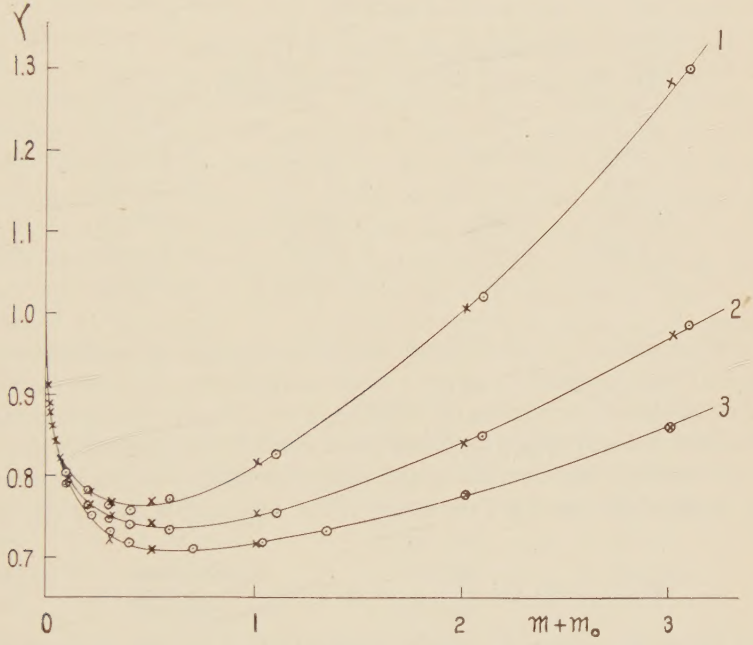

FIG. 1

Activity Coefficients of Hydrobromic Acid in Potassium and Sodium Bromide Solutions.

⊙ 0.1 M Acid Series
× 0.01 M Acid Series
1. HBr in NaBr
2. HBr in KBr
3. HCl in KCl.

Tables III and IV contain the results of the measurements of the above cells containing potassium hydroxide in potassium bromide solutions and potassium hydroxide in potassium iodide solutions, respectively. The first three columns show the concentrations of the solutions contained in the cells and the fourth column the observed electromotive forces. Since the exclusion of dissolved air was necessary which involved the process of boiling in vacuum,

[1] Harned: J. Am. Chem. Soc., 48, 326 (1926).

TABLE III

Electromotive Forces of the Cells:
$H_2 \mid KOH(m_2), KBr(m) \mid K_xHg \mid KOH(m_1) \mid H_2$

m_1	m_2	m	E	$\triangle E$	$E_{Corr.}$
0.1010	0.1009	0.2025	0.02263	0.00023	0.02286
0.1012	0.1014	0.5091	0.03767	0.00024	0.03791
0.1006	0.1008	1.012	0.05186	0.00003	0.05189
0.1008	0.1003	2.015	0.06899	0.00032	0.06931
0.1017	0.1007	3.103	0.08040	0.00067	0.08107

TABLE IV

Electromotive Forces of the Cells:
$H_2 \mid KOH(m_2), KI(m) \mid K_xHg \mid KOH(m_1) \mid H_2$

m_1	m_2	m	E	$\triangle E$	$E_{Corr.}$
0.1015	0.1016	0.2036	0.02152	0.00028	0.02175
0.1035	0.1025	0.5135	0.03565	0.00049	0.03614
0.1010	0.1019	1.022	0.05001	0.00001	0.05000
0.1031	0.1022	2.048	0.06668	0.00098	0.06766
0.1012	0.1012	3.044	0.07838	0.00029	0.07867

it was not convenient to make them up to exact round concentrations. For this reason, it was necessary to apply a small correction to the observed electromotive forces in order to obtain the electromotive forces of the cells containing exactly 0.1 M potassium hydroxide on both sides. This correction was made on the assumption that over the small ranges of concentration involved, the activity coefficients remained constant. The equation used for this correction is

$$\Delta E = 0.1183 \log \frac{m_1}{m_o} - 0.0591 \log \frac{m_2(m_2+m)}{m_o(m_o+m)} \qquad (3)$$

in which m_o is the desired hydroxide concentration (in the present instance 0.1 M) and ΔE the correction to be applied. In the fifth columns of Tables III and IV are given the values of ΔE and in the sixth the corrected electromotive forces.

These electromotive forces are related to the activities of the ions and water by the equation

$$E = 0.05915 \log \frac{\gamma_{K(s)}\gamma_{OH(s)}\, a_{H_2O(m_1)}\, (m+m_o)m_o}{\gamma_{K(0.1)}\gamma_{OH(0.1)}\, a_{H_2O(s)}\, m_o^2} \qquad (4)$$

whence

$$E + 0.02568 \ln \frac{a_{H_2O(s)}}{a_{H_2O(0.1)}} = 0.05915 \log \frac{\gamma_{K(s)}\gamma_{OH(s)}\,(m+0.1)}{\gamma_{K(0.1)}\gamma_{OH(0.1)}\,0.1} \qquad (5)$$

where the subscript "s" refers to the solution of concentration (m+0.1). Thus, if $\gamma_{K(0.1)}\gamma_{OH(0.1)}$ is known, $\gamma_{K(s)}\gamma_{OH(s)}$ and, therefore, $\gamma_{KOH(s)}$ or $\sqrt{\gamma_{K(s)}\gamma_{OH(s)}}$ may be calculated. Since the activity of water is proportional to its partial

vapor pressure, the second member on the left of this equation is equal to $0.02568 \ln p_s/p_{0.1}$. To compute the water activity ratios, the equation,

$$\ln \frac{p_o}{p_s} = \frac{m}{55.5}\left[2 + 2.303\,\alpha m - \frac{4.606\beta\alpha'}{\alpha'+1}\, m^{\alpha'}\right] \qquad (6)$$

which was shown by Harned[1] to be approximately valid over a considerable concentration range for strong uniunivalent electrolytes was found to be sufficiently accurate. p_o is the vapor pressure of pure water and p_s the vapor pressure of the solution. The values of the constants α, α', and β were obtained by the graphical method employed by Harned from the activity coefficients of potassium bromide and iodide which were calculated from the data of Pearce and Hart and Douglas. The values of the constants used were 0.08, 0.292, and 0.392 for α, β, and α' in the case of potassium bromide, and 0.075, 0.263, and 0.353 for potassium iodide. It was assumed that the vapor pressures of the solutions containing the potassium halide at concentrations (m) and 0.1 M potassium hydroxide were the same as those of the salt solutions at concentrations (m+0.1). The value of $\ln p_o/p_{0.1}$ was first computed, and then the values of $\ln p_o, p_s$ at round concentrations, whence $\ln p_s/p_{0.1}$ was obtained and, subsequently, $0.02568 \ln p_s/p_{0.1}$. These were plotted against the molal concentrations from which graphs the values in the third columns of Tables V and VI were obtained. The values of γ calculated by equation (5) are given in the fifth columns of these tables. 0.772 at 0.1 M was taken as reference value.[2]

TABLE V

The Activity Coefficient of Potassium Hydroxide in Potassium Bromide Solutions KOH = 0.1 M

m	E	$0.02568 \ln p_s/p_{0.1}$	$E+0.02568 \ln p_s/p_{0.1}$	γ
0.0000	0.00000	0.000000	0.00000	0.772
0.2025	0.02286	−0.000168	0.02269	0.690
0.5091	0.03791	−0.000423	0.03749	0.649
1.012	0.05189	−0.000850	0.05104	0.625
2.015	0.06931	−0.001755	0.06756	0.625
3.103	0.08107	−0.002856	0.07821	0.625

TABLE VI

The Activity Coefficient of Potassium Hydroxide in Potassium Iodide Solutions KOH = 0.1 M

m	E	$0.02568 \ln p_s/p_{0.1}$	$E+0.02568 \ln p_s/p_{0.1}$	γ
0.0000	0.00000	0.000000	0.00000	0.772
0.2036	0.02175	−0.000172	0.02158	0.674
0.5135	0.03614	−0.000437	0.03670	0.624
1.022	0.05000	−0.000881	0.04912	0.600
2.048	0.06766	−0.001861	0.06580	0.599
3.044	0.07867	−0.002925	0.07574	0.601

[1] Harned: J. Am. Chem. Soc., **44**, 252 (1922).

[2] Scatchard: J. Am. Chem. Soc., **47**, 648 (1925).

The activity coefficients of potassium hydroxide in potassium bromide and iodide solutions as well as the values obtained by Harned[1] for this hydroxide in potassium chloride solutions are plotted in Fig. 2 whence it is seen that the hydroxide has the lower activity coefficient in the solutions of the salt which has the higher activity coefficient. As far as we are aware, this behavior is a general one and is just opposite to the behavior of acids in the salt solutions. To sum up, it is found that the activity coefficient of an acid and also the hydrogen ion is greater at a given concentration in a solution of a salt which itself possesses the greater activity coefficient whereas the reverse is true for the hydroxyl ion and hydroxides.

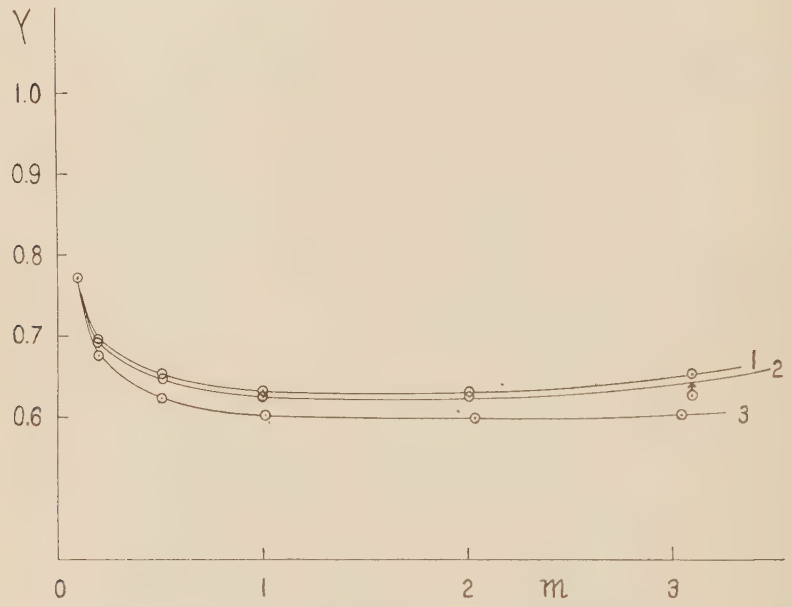

Fig. 2

The Activity Coefficient of KOH in KCl, KBr and KI Solutions.

1 KOH in KCl
2 KOH in KBr
3 KOH in KI

(5) The Ion Activity Coefficient and Ionic Concentration Product of Water in Potassium and Sodium Bromide Solutions.

The results of the measurements of the cells already described, together with the other data taken from the work of Douglas on cells of the type

$$Ag \mid AgBr \mid MBr(m_1) \mid M_xHg \mid MBr(m_2) \mid AgBr \mid Ag$$

permit the calculation of the activity coefficient of water as an electrolyte and the ionic concentration product of water in sodium and potassium bromide

[1] Harned: J. Am. Chem. Soc., 47, 689 (1925).

solutions by a method analogous to that used by Harned, Harned and Swindells, and Åkerlöf[1] for the alkaline chloride and sulphate solutions.

The electromotive forces of the cells of the type

$$Ag \mid AgBr \mid HBr(m_o), MBr(m) \mid H_2 \mid HBr(m_o) \mid AgBr \mid Ag$$

which are given in column five in Table I and II are related to the activity coefficients of the hydrogen and bromide ions by the equation

$$E_1 = 0.05915 \log \frac{\gamma_{H(s)}\gamma_{Br(s)}}{\gamma_{H(m_o)}\gamma_{Br(m_o)}} \frac{(m+m_o)m_o}{m_o^2} \qquad (1)$$

where the subscript "s" refers to the solution containing salt and acid, and m_o to the solution containing acid only. The electromotive forces of the cells

$$H_2 \mid MOH(m_o), MBr(m) \mid M_xHg \mid MOH(m_o) \mid H_2$$

are related to the activity coefficients of the metal and hydroxyl ions and activities of the water molecules by the equation

$$E_2 = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{OH(s)}\ a_{H_2O(m_o)}}{\gamma_{M(m_o)}\gamma_{OH(m_o)}\ a_{H_2O(s)}} \frac{(m_o+m)m_o}{m_o^2} \qquad (4)$$

Upon adding these two equations and rearranging the terms, we obtain

$$E_1+E_2 = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{Br(s)}}{\gamma_{M(m_o)}\gamma_{Br(m_o)}} \frac{(m+m_o)^2}{m_o^2} + 0.05915 \log \frac{\gamma_{H(s)}\gamma_{OH(s)}a_{H_2O(m_o)}}{\gamma_{H(m_o)}\gamma_{OH(m_o)}a_{H_2O(s)}} \qquad (7)$$

The electromotive forces of the cells

$$Ag \mid AgBr \mid MBr(m+m_o) \mid M_xHg \mid MBr(m_o) \mid AgBr \mid Ag$$

are given by the equation

$$E_3 = 0.05915 \log \frac{\gamma_{M(m+m_o)}\gamma_{Br(m+m_o)}}{\gamma_{M(m_o)}\gamma_{Br(m_o)}} \frac{(m+m_o)_2}{m^{2o}} \qquad (8)$$

It can be seen that the right-hand member of this equation is identical with the first member on the right of equation (7). Subtracting (8) from (7) and rearranging terms we obtain

$$E_1+E_2-E_3 = 0.05915 \log \frac{\dfrac{\gamma_{H(s)}\gamma_{OH(s)}}{a_{H_2O(s)}}}{\dfrac{\gamma_{H(m_o)}\gamma_{OH(m_o)}}{a_{H_2O(m_o)}}} = 0.05915 \log \frac{K_{\gamma(s)}}{K_{\gamma(m_o)}} \qquad (9)$$

The calculation is shown in Tables VII and VIII in the case of potassium bromide and in Tables IX and X for sodium bromide.

[1] Harned: J. Am. Chem. Soc., **47**, 830 (1925); Harned and Swindells: **48**, 126 (1926); Åkerlöf: 48, 1160 (1926).

Table VII

The Ionic Activity Coefficient Product of Water in Potassium Bromide Solutions
0.1 M Acid-Hydroxide Series

m+0.1	E_1	E_2	E_3	$E_1+E_2-E_3$	$K\gamma_{(s)}/K\gamma_{(0.1)}$
0.1	0.00000	0.0000	0.0000	0.0000	1.000
0.2	0.01518	0.0141	0.0323	−0.0030	0.890
0.3	0.02438	0.0227	0.0513	−0.0042	0.848
0.4	0.03128	0.0287	0.0643	−0.0043	0.846
0.6	0.04126	0.0372	0.0830	−0.0045	0.839
1.1	0.05832	0.0511	0.1110	−0.0016	0.940
2.1	0.08102	0.0687	0.1435	0.0061	1.268
3.1	0.09816	0.0801	0.1637	0.0126	1.633

Table VIII

$\gamma_H\gamma_{OH}/a_{H_2O}$, $\sqrt{\gamma_H\gamma_{OH}}$, and m_w of Water in Potassium Bromide Solutions

m+0.1	$K\gamma_{(s)}=\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$	$0.02568 \ln p_s/p_{0.1}$	$E_4=0.1183 \log \gamma_s/\gamma_{0.1}$	$\gamma_s=\sqrt{\gamma_H\gamma_{OH}}$	$m_w\times 10^7$
0.1	0.569	0.000000	0.00000	0.754	1.329
0.2	0.507	−0.000085	−0.00309	0.710	1.408
0.3	0.484	−0.000167	−0.00437	0.693	1.442
0.4	0.482	−0.000248	−0.00455	0.690	1.445
0.6	0.478	−0.000414	−0.00491	0.685	1.450
1.1	0.535	−0.000842	−0.00244	0.719	1.371
2.1	0.721	−0.001741	0.00436	0.821	1.180
3.1	0.842	−0.002746	0.00985	0.913	1.093

Table IX

The Ionic Activity Coefficient Product Ratio of Water in Sodium Bromide Solutions
0.1 M Acid-Hydroxide Series

m+0.1	E_1	E_2	E_3	$E_1+E_2-E_3$	$K\gamma_{(s)}/K\gamma_{(0.1)}$
0.1	0.00000	0.0000	0.0000	0.0000	1.000
0.2	0.01572	0.0139	0.0331	−0.0035	0.873
0.3	0.02541	0.0225	0.0524	−0.0045	0.839
0.4	0.03260	0.0285	0.0663	−0.0052	0.817
0.6	0.04374	0.0372	0.0862	−0.0053	0.814
1.1	0.06297	0.0516	0.1175	−0.0029	0.893
2.1	0.09049	0.0697	0.1546	0.0056	1.244

TABLE X

$\gamma_H\gamma_{OH}/a_{H_2O}$, $\sqrt{\gamma_H\gamma_{OH}}$, and m_w of Water in Sodium Bromide Solutions

m+0.1	$K\gamma s = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$	0.02568 ln $p_s/p_{0.1}$	$E_4 = 0.1183 \log \gamma_s/\gamma_{0.1}$	$\gamma_s = \sqrt{\gamma_H\gamma_{OH}}$	$m_w \times 10^7$
0.1	0.551	0.000000	0.00000	0.742	1.351
0.2	0.481	−0.000085	−0.00358	0.692	1.445
0.3	0.462	−0.000169	−0.00467	0.678	1.475
0.4	0.450	−0.000256	−0.00676	0.663	1.494
0.6	0.449	−0.000428	−0.00573	0.664	1.497
1.1	0.492	−0.000893	−0.00379	0.689	1.429
2.1	0.685	−0.001963	0.00364	0.796	1.211

Tables VII and IX contain in the first columns the molal concentrations, and in the next three columns the values of E_1, E_2 and E_3. The values of E_1 are those given in the fifth columns of Tables V and VI, respectively. The values of E_2 for potassium bromide were read off from large scale plots of the values given in the second column of Table V. In the case of sodium bromide the values shown for E_2 in Table IX were obtained in the same manner from the data of Douglas on sodium hydroxide in sodium bromide solutions. The values of E_3 for both neutral salt solutions were also derived from the work of Douglas by reading off the values at the required concentrations from large scale plots. In the fifth columns of Tables VII and IX are given the values of $E_1+E_2-E_3$ and in the sixth columns the values of $K_{\gamma(s)}/K_{\gamma(0.1)}$ calculated by means of equation (9). We have now to estimate $K_{\gamma(0.1)}$ in order to compute the absolute values of $K_{\gamma(s)}$ and of the activity coefficient of water as an electrolyte, γ_s or $\sqrt{\gamma_H\gamma_{OH}}$. Since our chief interest lies in the comparison of these results with those obtained by Harned[1] on the ionic concentration of water in potassium and sodium chloride solutions, we have simply taken $K_{\gamma(0.1)}$ at the reference concentration, 0.1M, to be somewhat less than the values employed in the case of the chloride solutions. Therefore, we let $\gamma_{0.1}$ equal 0.754 and 0.742 for potassium and sodium bromides at 0.1 M, whereas Harned employed 0.764 and 0.752 for the respective chlorides. From these values, $K_{\gamma(0.1)}$ is found to be 0.569 and 0.551 for the potassium and sodium bromide solutions, respectively.

In the second columns of Tables VIII and X are given the values of $K_{\gamma(s)}$ calculated from the ratios in the sixth columns of Table VII and IX. In order to compute γ_s or $\sqrt{\gamma_H\gamma_{OH}}$ it is necessary to eliminate a_{H_2O}. This has been done by the method previously employed in the calculation of the activity coefficient of the hydroxide in the bromide and iodide solutions. The third columns of Tables VIII and X contain the values of 0.02568 ln $p_s/p_{0.1}$ obtained by readings at the required concentrations from the appropriate large scale plots. The fourth columns of Tables VIII and X contain the values of E_4 obtained by adding the values of 0.02568 ln $p_s/p_{0.1}$ to those given in the fifth

[1] Harned: J. Am. Chem. Soc., 47, 930 (1925).

columns of Tables VII and IX. The fifth columns in Tables VIII and X contain the values of γ_s calculated from the values of E_4 by means of the equation

$$E_4 = 0.1183 \log \gamma_s/\gamma_{0.1} \qquad (10)$$

The results obtained also permit the calculation of the dissociation of water, or the molal concentration of dissociated water molecules per 1000 gs.

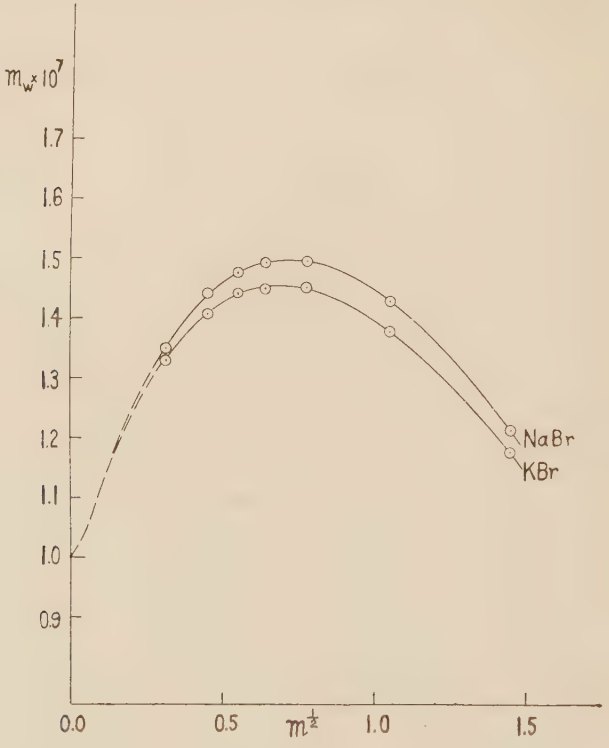

FIG. 3

The Dissociation of Water in Potassium and Sodium Bromide Solutions.

of water, m_w. The constant of equilibrium for the dissociation of water into ions is given thermodynamically by

$$K_w = \frac{a_H a_{OH}}{a_{H_2O}} = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_w^2$$

where k_w is the dissociation constant, and m_w the concentration of the hydrogen and hydroxyl ions of water. Solving for m_w, we obtain

$$m = m_H = m_{OH} = \sqrt{\frac{K_w}{K_{\gamma(s)}}} \qquad (11)$$

The value of K_w at 25° was taken to be 1.005×10^{-14}. The values of m $\times 10^7$ are shown in the sixth columns of Tables VIII and X.

In Fig. 3, the values of $m_w \times 10^7$ in potassium and sodium bromide solutions are plotted against the square root of the salt concentration. The

dashed curves at salt concentrations below 0.1 M were not determined but were estimated from the similar results obtained by Harned[1] in the cases of the corresponding chloride solutions. These plots are quite similar to those obtained by Harned, and are of the same order of magnitude. Sodium bromide produces a somewhat greater dissociation than potassium bromide and sodium chloride, and potassium bromide produces a somewhat greater dissociation than potassium chloride. The maxima of all these curves occur at approximately 0.5 M salt concentration.

Summary

(1) Measurements of the following types of cells were made:

H_2 | KOH(m_o), KBr(m) | K_xHg | KOH(m_o) | H_2
H_2 | KOH(m_o), KI(m) | K_xKg | KOH(m_o) | H_2
H_2 | KBr(m_o), KBr(m) | AgBr | Ag
H_2 | HBr(m_o), NaBr(m) | AgBr | Ag

(2) From the results obtained, the activity coefficients of potassium hydroxide in solutions of potassium bromide and iodide, and of hydrobromic acid in solutions of potassium and sodium bromides have been calculated.

(3) A calculation of the activity coefficient of water as an electrolyte and the ionic concentration of water in potassium and sodium bromide solutions has been made.

Philadelphia,
Pennsylvania.

---

[1] Harned: J. Am. Chem. Soc., **47**, 930 (1925).